

Molecular zero-range potential method and its application to cyclic structures

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Abstract

The zero-range potentials of the radial Schrodinger equation are investigated from a point of Darboux transformations scheme. The dressing procedure is realized as a sequence of Darboux transformations in a way similar to that used to obtain the generalized zero-range potentials of Huang-Derevianko by specific choice of a family of parameters. In the present approach we stay within the framework of conventional zero-range potential method whilst the potential parameter (scattering length) is modified taken into account spectral molecular properties. This allows to introduce molecular zero-range potential once the corresponding discrete spectrum is known. The results are illustrated on example of flat cyclic molecular structures, with particular focus on a benzene molecule, which bounded states energies are first found using atomic zero-range potentials, compared with the Huckel method, and then used to introduce single zero-range potential describing the entire molecule. Reasonable scattering behavior for newly introduced potential gives a possibility to tackle many-molecule problems representing molecules as appropriate single zero-range potentials.

1 Introduction

Zero-range potential (ZRP) method is proved to be an efficient tool in describing quantum structures with arbitrary geometry at sufficiently low energies such that detailed structure and interactions of atoms (replaced with point-centers) between themselves can be neglected [13, 5, 2, 9, 12]. Simplicity of the approach makes it very attractive and over the years it has been further developed into generalized zero-range potential (gZRP) method that takes into account effects of higher order partial waves in describing scattering properties [14, 15, 10, 4, 18, 19, 16]. However, the scope of application of the regular ZRP method can be extended to describe not only small, typically atomic, structures but larger molecular systems.

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In the present work, after giving brief but self-consistent review of Darboux transformation (DT) and gZRP ideas, we enhance standard ZRP approach by means of application of a dressing procedure [11, 18, 19]. We notice and make use the fact that a certain class of DTs of spherically symmetric ZRPs yields also a potential of zero range but, in general, with different effective characteristic (s -wave scattering length of the original ZRP is altered). Transformation parameters of a single atomic potential can be chosen based on solution of conventional bounded state problem solved for a system of ZRPs (molecule) such that resulting solution mimics scattering behavior for the molecule as a whole at low energies.

Described ZRP treatment is demonstrated on example of a generic cyclic structure with focus on a particular case of benzene molecule.

2 Method of zero-range potentials

The idea of the ZRP method is to replace real potential with a point potential placed in the origin that mimics physical scattering behavior in the far zone.

Therefore the equation in question is the radial Schrodinger equation for the free space ($r > 0$)

$$-\left(\psi'' + \frac{2}{r}\psi'\right) + \frac{l(l+1)}{r^2}\psi = k^2\psi, \quad (1)$$

where $k^2 = \frac{2\mu E}{\hbar^2}$ is wave number, μ , E are mass and energy of a particle (electron), respectively, \hbar is the Planck's constant, $\psi = \psi(r)$ is the radial part of the wave function.

It is well-known that the general solution can be formed as a linear combination of spherical Bessel and Neumann functions, $j_l(kr)$ and $y_l(kr)$, respectively,

$$\psi(r) = C_l (j_l(kr) - \tan \eta_l \cdot y_l(kr)), \quad (2)$$

or as a combination of spherical Hankel functions

$$\psi(r) = \tilde{C}_l \left(s_l h_l^{(1)}(kr) - h_l^{(2)}(kr) \right), \quad (3)$$

with $s_l = \exp(2i\eta_l)$ being a scattering matrix.

Taking into account the following asymptotes at $kr \rightarrow 0$ [1]

$$j_l(kr) \approx \frac{(kr)^l}{(2l+1)!!}, \quad (4)$$

$$y_l(kr) \approx -\frac{(2l-1)!!}{(kr)^{l+1}}, \quad (5)$$

written with notion of the odd factorial $(2l+1)!! = (2l+1) \cdot (2l-1) \cdot \dots \cdot 3 \cdot 1$, $(-1)!! = 1$, we obtain asymptotic behavior of finite-energy solution at the origin

$$\psi(r) \approx C_l \left(\frac{(kr)^l}{(2l+1)!!} + \tan \eta_l \frac{(2l-1)!!}{(kr)^{l+1}} \right) \approx C_l \tan \eta_l \frac{(2l-1)!!}{(kr)^{l+1}}. \quad (6)$$

From here, the constant C_l can be expressed as

$$C_l = \frac{(2l+1)!!}{k^l (2l+1)!} \left. \frac{d^{2l+1}}{dr^{2l+1}} (r^{l+1} \psi) \right|_{r=0}. \quad (7)$$

Elimination of C_l yields

$$\frac{1}{r^{l+1} \psi} \frac{d^{2l+1}}{dr^{2l+1}} (r^{l+1} \psi) \Big|_{r=0} = \frac{(2l+1)!}{(2l+1)!!} \cdot \frac{1}{(2l-1)!!} \cdot \frac{k^{2l+1}}{\tan \eta_l}, \quad (8)$$

This is to say that imposing the boundary condition

$$\frac{1}{r^{l+1} \psi} \frac{d^{2l+1}}{dr^{2l+1}} (r^{l+1} \psi) \Big|_{r=0} = -\frac{2^l l!}{(2l-1)!!} 1/a_l^{2l+1}, \quad (9)$$

with

$$a_l^{2l+1} = -\frac{\tan \eta_l}{k^{2l+1}}. \quad (10)$$

results in the desired physical behavior of solution at far distance from the point-center.

Introduced quantity a_l is termed as the partial wave scattering length and is independent of particular energy value at low energies. To justify this fact, it is enough to consider zero-energy solution to the equation (1)

$$\psi(r) = A_1 r^l + A_2 \frac{1}{r^{l+1}}.$$

By matching this with (2), we conclude

$$\tan \eta_l \approx \underbrace{-A_2/A_1 \frac{1}{(2l+1)!! (2l-1)!!}}_{\text{const}} k^{2l+1},$$

that demonstrates energy-independence of scattering length parameters a_l .

In most of the cases, at low energies, it is enough to consider ZRP as a spherical point, thus neglecting higher partial waves. Therefore, solution to the (1) should be a subject to the simple boundary condition

$$\left. \frac{d \log (r \psi)}{dr} \right|_{r=0} = -\beta, \quad (11)$$

where $\beta = 1/a_0$ is the s -wave inverse scattering length.

3 Darboux transformation and its application

Consider one-dimensional Sturm-Liouville equation

$$L\psi = \lambda\psi, \quad (12)$$

where

$$L = -\frac{d^2}{dx^2} + u(x). \quad (13)$$

Now we apply such algebraic-differential transformation (referred as Darboux transformation [8])

$$D = \frac{d}{dx} - \sigma(x) \quad (14)$$

that the transformed equation preserve the same form

$$L^{[1]}\psi^{[1]} = \lambda\psi^{[1]}, \quad (15)$$

where $\psi^{[1]} = D\psi$, $L^{[1]} = -\frac{d^2}{dx^2} + u^{[1]}(x)$ and the transformed potential is

$$u^{[1]}(x) = u(x) - 2\sigma'(x). \quad (16)$$

It is straightforward to check that

$$\sigma(x) = \frac{\Phi_1'}{\Phi_1} \quad (17)$$

with Φ_1 being a particular solution to the original equation, i.e. it satisfies

$$-\Phi_1'' + u(x)\Phi_1 = \lambda_1\Phi_1$$

for some λ_1 .

It can be shown that in case of multiple application of the Darboux transformation, the expression (17) is generalized into

$$\sigma(x) = \frac{d}{dx} [\log W(\Phi_1, \dots, \Phi_N)]$$

resulting in the following transformation of the potential

$$u^{[N]}(x) = u(x) - 2 \frac{d^2}{dx^2} [\log W(\Phi_1, \dots, \Phi_N)]. \quad (18)$$

Corresponding transformation of the solution is given by the Crum's formula [7, 20]

$$\psi^{[N]} = D^{[N]} \psi = \frac{W(\Phi_1, \dots, \Phi_N, \psi)}{W(\Phi_1, \dots, \Phi_N)}, \quad (19)$$

where W denote determinants of the Wronskian matrices.

Having considered one-dimensional Cartesian case, we move towards the radial Schrodinger equation (1) and notice that it can be brought to the form (12) eligible for direct application of obtained transformation formulas. Namely, performing substitution $\psi = \chi/r$, one readily obtains

$$-\chi'' + \frac{l(l+1)}{r^2} \chi = k^2 \chi. \quad (20)$$

That is to say, that we can apply Darboux transformation to the equation (1) meaning that all original wave functions ψ should be multiplied by r whereas the potential term

$$u(r) = \frac{l(l+1)}{r^2} \quad (21)$$

remains unchanged.

Thus, the formulas (18), (23) in spherical coordinates should be replaced with

$$u^{[N]}(r) = u(r) - 2 \frac{d^2}{dr^2} [\log W(r\Phi_1, \dots, r\Phi_N)] \quad (22)$$

and

$$\psi^{[N]} = D^{[N]} \psi = \frac{W(r\Phi_1, \dots, r\Phi_N, r\psi)}{rW(r\Phi_1, \dots, r\Phi_N)}. \quad (23)$$

Following an idea of the previous works [11], we first show how gZRP can be induced by application of DT.

We start by choosing a spherical Bessel function as the seed solution

$$\psi_l(r) = j_l(kr) \quad (24)$$

and apply N -th order Darboux transformation by taking spherical Hankel functions with specific parameters κ_m as prop functions

$$\Phi_m(r) = h_l^{(1)}(-i\kappa_m r), \quad m = 1, \dots, N. \quad (25)$$

We can employ Crum's formula (19) and consider asymptotic behavior of spherical functions at $r \rightarrow \infty$

$$j_l(kr) \approx \frac{\sin(kr - l\pi/2)}{kr}, \quad (26)$$

$$y_l(kr) \approx -\frac{\cos(kr - l\pi/2)}{kr}, \quad (27)$$

$$h_l^{(1)}(kr) = j_l(kr) + iy_l(kr) \approx (-i)^{l+1} \frac{\exp(ikr)}{kr}, \quad (28)$$

$$h_l^{(2)}(kr) = j_l(kr) - iy_l(kr) \approx i^{l+1} \frac{\exp(-ikr)}{kr}. \quad (29)$$

Then the Wronskians turn into Vandermonde determinants, hence,

$$\psi_l^{[N]}(r) = C \left[(-i)^l \frac{\exp(ikr)}{kr} \frac{\Delta(\kappa_1, \dots, \kappa_N, ik)}{\Delta(\kappa_1, \dots, \kappa_N)} - i^l \frac{\exp(-ikr)}{kr} \frac{\Delta(\kappa_1, \dots, \kappa_N, -ik)}{\Delta(\kappa_1, \dots, \kappa_N)} \right], \quad (30)$$

where C represents here and later on a generic constant without prescribing it any specific value such that it can absorb constant multipliers where their meaning is not important without changing notation.

We note that for $l = 0$ this expression is not asymptotic, but exact.

A Vandermonde determinant in (30) can be computed by noticing that $k = -i\kappa_m$ (for $m = 1, \dots, N$) are the roots of polynomial with respect to k equation that is obvious due to the fact that replacement $ik \rightarrow \kappa_m$ yields zero determinant due to linear dependencies of the rows, thereby allowing the following factorization

$$\Delta(\kappa_1, \dots, \kappa_N, ik) = \begin{vmatrix} 1 & \kappa_1 & \kappa_1^2 & \dots & \kappa_1^N \\ 1 & \kappa_2 & \kappa_2^2 & \dots & \kappa_2^N \\ \dots & \dots & \dots & \dots & \dots \\ 1 & \kappa_N & \kappa_N^2 & \dots & \kappa_N^N \\ 1 & ik & (ik)^2 & \dots & (ik)^N \end{vmatrix} = C \prod_{m=1}^N (\kappa_m - ik).$$

Denoting

$$s_l = \prod_{m=1}^N \frac{(\kappa_m - ik)}{(\kappa_m + ik)} = - \prod_{m=1}^N \frac{(k + i\kappa_m)}{(k - i\kappa_m)}, \quad (31)$$

we recognize in the expression (30) the asymptotes of spherical Hankel functions, hence

$$\psi_l^{[N]}(r) = C \left[s_l h_l^{(1)}(kr) - h_l^{(2)}(kr) \right]. \quad (32)$$

As one can notice, the expression (32) coincides with (3) if

$$\exp(2i\eta_l) = \prod_{m=1}^N \frac{(\kappa_m - ik)}{(\kappa_m + ik)}, \quad (33)$$

or, taking into account (10),

$$\tan \eta_l = -a_l^{2l+1} k^{2l+1} = -i \frac{\prod_{m=1}^N (\kappa_m - ik) - \prod_{m=1}^N (\kappa_m + ik)}{\prod_{m=1}^N (\kappa_m - ik) + \prod_{m=1}^N (\kappa_m + ik)}. \quad (34)$$

Thus we conclude that for the direct correspondence to the gZRP behavior, the number of consequent transformations $N = 2l + 1$ should be taken.

Given some quantity $a = |a| e^{i\phi_a}$, the parameters $\kappa_1, \dots, \kappa_{2l+1}$ needs to be chosen in a way that

$$\prod_{m=1}^{2l+1} (\kappa_m + ik) = (ik)^{2l+1} - a. \quad (35)$$

This is equivalent to the $ik = -\kappa_m$ ($m = 1, \dots, 2l + 1$) being the roots of the equation

$$(ik)^{2l+1} = a,$$

that is to say $-\kappa_m = \sqrt[2l+1]{a}$, or

$$-\kappa_m = |a|^{1/(2l+1)} \exp\left(i \frac{(\phi_a + 2\pi m)}{2l+1}\right), \quad m = 1, \dots, 2l+1. \quad (36)$$

In the similar manner we obtain

$$\prod_{m=1}^{2l+1} (\kappa_m - ik) = (-ik)^{2l+1} - a. \quad (37)$$

Substitution of (35), (37) into (34) results in

$$a = (-1)^{l+1} / a_l^{2l+1}.$$

Therefore, providing a_l is a real number, (36) yields

$$\kappa_m = -1/a_l \cdot \exp\left(i\pi \frac{l+2m+1}{2l+1}\right), \quad m = 1, \dots, 2l+1. \quad (38)$$

Now alternatively to gZRP instead of taking into account impact of higher harmonics, we consider the transformation of spherically symmetric solution (i.e. $l = 0$) with the parameters κ_m to be chosen according to spectral data of the entire molecule obtained, for example, from the discrete spectrum of molecule modeled by regular ZRP method.

We get back to (34) and since

$$\prod_{m=1}^N (\kappa_m + ik) = \prod_{m=1}^N \kappa_m + ik \sum_{n=1}^N \prod_{\substack{m=1 \\ m \neq n}}^N \kappa_m + (ik)^2 \sum_{j=1}^N \sum_{n < j}^N \prod_{\substack{m=1 \\ m \neq n, m \neq j}}^N \kappa_m + \dots + (ik)^{N-1} \sum_{n=1}^N \kappa_n + (ik)^N,$$

we continue the last equality as

$$a_l^{2l+1} k^{2l+1} = -i \frac{ik \sum_{n=1}^N \prod_{\substack{m=1 \\ m \neq n}}^N \kappa_m + \dots + (ik)^N}{\prod_{m=1}^N \kappa_m + \dots + (ik)^{N-1} \sum_{n=1}^N \kappa_n}. \quad (39)$$

Limiting ourselves with $l = 0$ case, we consider low-energy limit neglecting terms of higher order than one with respect to k to obtain

$$a_0 = \frac{\sum_{n=1}^N \prod_{\substack{m=1 \\ m \neq n}}^N \kappa_m}{\prod_{m=1}^N \kappa_m}. \quad (40)$$

Alternatively, recalling notation $\beta = 1/a_0$, the last expression can be rewritten as

$$\beta = \left(\sum_{m=1}^N \kappa_m^{-1} \right)^{-1} \quad (41)$$

On the other hand, we can readily observe that Darboux transformation of the seed solution (24) with the prop functions (25) results in the solution corresponding to the ZRP for arbitrary choice of N and parameters κ_m , $m = 1, \dots, N$. Indeed, for $l = 0$

$$\log W(r\Phi_1, \dots, r\Phi_N) = \sum_{m=1}^N \kappa_m r + C,$$

thus, according to (22),

$$u^{[N]}(r) \equiv 0, \quad r > 0.$$

Freedom of choice of transformation parameters gives a possibility to induce desired poles of scattering matrix (31) and, thereby, perform transition from atomic to molecular ZRP by choosing κ_m , $m = 1, \dots, M$ such that new potential allows M bounded states obtained by solving conventional formulation of the discrete spectrum problem for the set of M standard ZRPs making up the molecule. Molecular ZRP can be qualitatively characterized by effective scattering length computed according to (40) and thus used in such simplified scattering calculations in complicated problems involving, for example, a chain of molecules.

Below we demonstrate the presented approach by applying it to a general cyclic molecule with eventual focus on a benzene molecule.

4 Case study: a cyclic molecule

In order to describe a cyclic structure, we consider a system (molecule) of M point-centers, typically atoms, modeled by ZRPs which positions are kept fixed in the plane in space in a cyclic order.

Spatial coordinates are chosen such that all atoms lie in the xy -plane with the origin coinciding with the center of the molecule. Atoms are numerated counterclockwise and the x -axis is chosen along the direction to the first atom. Described geometry is illustrated on the Fig. 1.

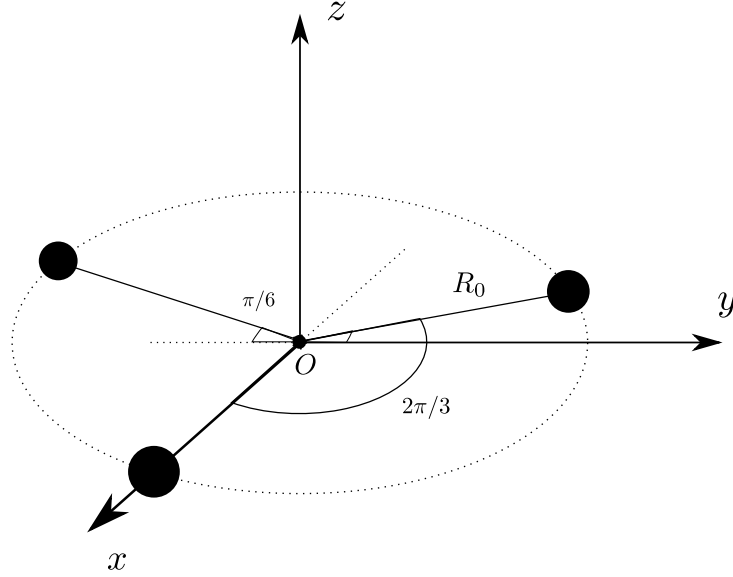


Fig. 1: Illustration of the geometry by an example of 3 atoms.

4.1 Bounded state problem

According to the idea of ZRP method, we write solution to the bounded state problem as

$$\psi(\vec{r}) = \sum_{j=1}^M C_j \cdot g\left(\left|\vec{r} - \vec{R}_j\right|, \kappa\right), \quad (42)$$

subject to the conditions (11)

$$\left. \frac{\partial \log\left(\left|\vec{r} - \vec{R}_i\right| \cdot \psi(\vec{r})\right)}{\partial \left|\vec{r} - \vec{R}_i\right|} \right|_{\left|\vec{r} - \vec{R}_i\right|=0} = -\beta, \quad i = 1, \dots, M, \quad (43)$$

where

$$g(r, \kappa) = \frac{e^{-\kappa r}}{r}. \quad (44)$$

Let us introduce the following notation. We will denote a distance between nearest neighboring atoms as ΔR_1 ,

between every second atom from each given one as ΔR_2 , every third as ΔR_3 , and so on (see the Fig. 2).

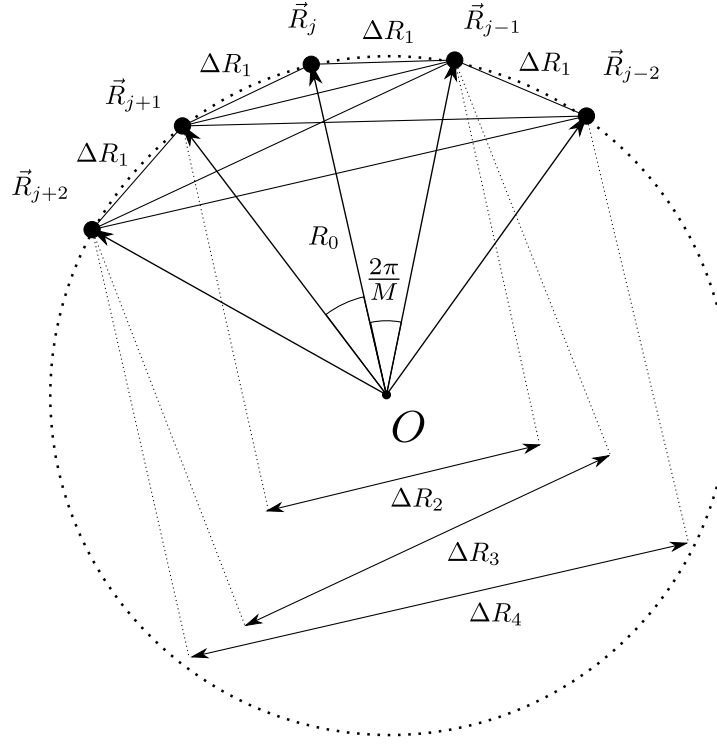


Fig. 2: Illustration of the distance notation.

From simple geometrical considerations it follows that

$$\Delta R_j = 2R_0 \sin \left(\frac{2\pi}{M} \cdot \frac{j}{2} \right) = 2R_0 \sin (\phi_{j+1}/2), \quad (45)$$

where $\phi_j = \frac{2\pi}{M} (j-1)$ is azimuthal angular coordinate of a j -th atom, R_0 is radius of the molecule. We note that the expression is formally valid for $j = 1, \dots, M$, however we note that there is only $[M/2]$ different values since $\Delta R_{[M/2]-j} = \Delta R_{[M/2]+j}$ for $j = 1, \dots, [M/2] - 1$ where $[\cdot]$, here and later on, marks integer part of an argument (i.e. the floor function).

We develop conditions (43) to show existence of the derivatives

$$\begin{aligned} \left. \frac{\partial \log \left(\left| \vec{r} - \vec{R}_i \right| \cdot \psi(\vec{r}) \right)}{\partial \left| \vec{r} - \vec{R}_i \right|} \right|_{\left| \vec{r} - \vec{R}_i \right|=0} &= \frac{1}{C_i} [(\dots + C_{i-1} \cdot g(\Delta R_1, \kappa) - C_i \cdot \kappa + C_{i+1} \cdot g(\Delta R_1, \kappa) + \dots) + \\ &+ \left| \vec{r} - \vec{R}_i \right| \cdot \left. \frac{\partial \left(\psi(\vec{r}) - g \left(\left| \vec{r} - \vec{R}_i \right|, \kappa \right) \right)}{\partial \left| \vec{r} - \vec{R}_i \right|} \right|_{\left| \vec{r} - \vec{R}_i \right|=0} \right]. \end{aligned}$$

To show that the last term in the square bracketed expression is well-defined and equal to zero due to the

presence of the multiplier $|\vec{r} - \vec{R}_i|$, we first note that $\psi(\vec{r}) - g(|\vec{r} - \vec{R}_i|, \kappa)$ is a function of the arguments $|\vec{r} - \vec{R}_j|$ for $j = 1, \dots, N, j \neq i$, which does not lead to a singularity when computed at $|\vec{r} - \vec{R}_i| = 0$. Thus, due to the chain rule, it remains to demonstrate that the derivatives $\frac{\partial |\vec{r} - \vec{R}_j|}{\partial |\vec{r} - \vec{R}_i|}$ do not blow up at $|\vec{r} - \vec{R}_i| = 0$. This can be done in a straightforward manner as it follows

$$\begin{aligned} \frac{\partial |\vec{r} - \vec{R}_j|}{\partial |\vec{r} - \vec{R}_i|} &= \frac{\partial |\vec{r} - \vec{R}_i + \Delta \vec{R}_{ij}|}{\partial |\vec{r} - \vec{R}_i|} = \frac{\partial \sqrt{|\vec{r} - \vec{R}_i|^2 + 2 \cdot (\Delta \vec{R}_{ij}, \vec{r} - \vec{R}_i) + |\Delta \vec{R}_{ij}|^2}}{\partial |\vec{r} - \vec{R}_i|} = \\ &= \frac{1}{|\vec{r} - \vec{R}_j|} \left(|\vec{r} - \vec{R}_i| + \frac{d(\Delta \vec{R}_{ij}, \vec{r} - \vec{R}_i)}{d|\vec{r} - \vec{R}_i|} \right), \end{aligned}$$

where $\Delta \vec{R}_{ij} = \vec{R}_i - \vec{R}_j$.

Taking into account that

$$\left. \frac{d(\Delta \vec{R}_{ij}, \vec{r} - \vec{R}_i)}{d|\vec{r} - \vec{R}_i|} \right|_{|\vec{r} - \vec{R}_i|=0} = \lim_{|\vec{\delta}| \rightarrow 0} \frac{(\Delta \vec{R}_{ij}, \vec{\delta}) - 0}{|\vec{\delta}|} = |\Delta \vec{R}_{ij}| \cdot \cos \alpha_{ij},$$

where $\cos \alpha_{ij} = \frac{(\Delta \vec{R}_{ij}, \vec{\delta})}{|\Delta \vec{R}_{ij}| \cdot |\vec{\delta}|}$, we conclude

$$\left. \frac{\partial |\vec{r} - \vec{R}_j|}{\partial |\vec{r} - \vec{R}_i|} \right|_{|\vec{r} - \vec{R}_i|=0} = \cos \alpha_{ij},$$

thus, we have shown the required boundedness

$$-1 \leq \left. \frac{\partial |\vec{r} - \vec{R}_j|}{\partial |\vec{r} - \vec{R}_i|} \right|_{|\vec{r} - \vec{R}_i|=0} \leq 1.$$

Therefore, eventually,

$$\left. \frac{\partial \log(|\vec{r} - \vec{R}_i| \cdot \psi(\vec{r}))}{\partial |\vec{r} - \vec{R}_i|} \right|_{|\vec{r} - \vec{R}_i|=0} = \frac{1}{C_i} (\dots + C_{i-1} \cdot g(\Delta R_1, \kappa) - C_i \cdot \kappa + C_{i+1} \cdot g(\Delta R_1, \kappa) + \dots) = -\beta$$

for $i = 1, \dots, M$.

This gives the set of homogeneous linear algebraic equations allowing to determine C_1, \dots, C_M while its compatibility condition yields spectral equation with respect to κ .

Alternatively, the set of constants can be found from general symmetrical considerations and spectral condition will follow from their direct substitution into the last equation taken, for instance, at $i = 1$. Thus the spectral

condition reads

$$\beta - \kappa + \sum_{j=1}^{M-1} C_{j+1}/C_1 \cdot g(\Delta R_j, \kappa) = 0. \quad (46)$$

To find all constants C_j employing symmetry of the problem, we introduce cyclic permutation operator T which action on the wave function (42) results in the replacement $\vec{R}_1 \rightarrow \vec{R}_2, \vec{R}_2 \rightarrow \vec{R}_3, \dots, \vec{R}_M \rightarrow \vec{R}_1$. Since $T^M \psi(\vec{r}) = \psi(\vec{r})$, we immediately find the operator eigenvalues

$$\lambda_n = \exp(2\pi i n/M), \quad n = 0, \dots, M-1, \quad (47)$$

where i here, and onwards in the similar combinations, stands for the imaginary unit $i = \sqrt{-1}$.

To proceed with corresponding set of constants, as a calculation trick, we assume an observation point to be arbitrary but close to the center of the molecule i.e. $r \ll R_0$ such that we can do approximation $e^{-\kappa|\vec{r}-\vec{R}_j|} \approx e^{-\kappa R_0}$ and write the following expansions

$$\frac{1}{|\vec{r} - \vec{R}_j|} = \sum_{l=0}^{\infty} \frac{r^l}{R_0^{l+1}} P_l(\cos \gamma_j), \quad j = 1, \dots, M, \quad (48)$$

where $\cos \gamma_j = \frac{\vec{r} \cdot \vec{R}_j}{|\vec{r}| \cdot R_0}$.

The addition theorem for spherical harmonics (e.g. [3]) allows to write

$$P_l(\cos \gamma_j) = \frac{4\pi}{2l+1} \sum_{m=-l}^l (-1)^m \cdot Y_l^m(\theta, \phi) \cdot Y_l^{-m}(\pi/2, 0) \cdot e^{-i(j-1)\frac{2\pi m}{M}} \quad (49)$$

Substitution of (42), (47)-(49) into the eigenvalue problem

$$T\psi(\vec{r}) = \lambda_n \psi(\vec{r})$$

yields

$$\sum_m \sum_{j=1}^M C_j e^{-ik\frac{2\pi m}{M}} = e^{i\frac{2\pi n}{M}} \sum_m \sum_{j=1}^M C_j e^{-i(j-1)\frac{2\pi m}{M}},$$

that is equivalent to

$$\begin{cases} \sum_m \sum_{j=1}^M C_j e^{-ij\frac{2\pi m}{M}} = e^{i\frac{2\pi n}{M}} \sum_m \sum_{j=1}^M C_{j+1} e^{-ij\frac{2\pi m}{M}} \\ C_{M+1} = C_1 \end{cases}.$$

This allows to conclude

$$C_{j+1} = e^{-i\frac{2\pi n}{M}} C_j,$$

and, consequently,

$$C_{j+1} = e^{-ij\frac{2\pi n}{M}} C_1, \quad j = 1, \dots, M-1, \quad n = 0, \dots, M-1. \quad (50)$$

Feeding this into (46) solves the problem of finding energy levels

$$E_n = -\frac{\hbar^2 \kappa_n^2}{2\mu}, \quad n = 0, \dots, [M/2]. \quad (51)$$

by treating transcendental equation with respect to κ_n (by means of numerical methods, e.g. the Newton-Raphson algorithm)

$$\beta - \kappa_n + \sum_{j=1}^M e^{-ij\frac{2\pi n}{M}} \cdot g(\Delta R_j, \kappa_n) = 0. \quad (52)$$

Structure of the spectrum is as it follows. Ground state $n = 0$ and the state with highest energy $n = M/2$ (in case of even number of atoms M) are the only non-degenerate ones,

$$\psi_0(\vec{r}) = C_1 \sum_{j=1}^M g\left(\left|\vec{r} - \vec{R}_j\right|, \kappa\right), \quad (53)$$

$$\psi_{M/2}(\vec{r}) = C_1 \sum_{j=1}^M (-1)^{j-1} \cdot g\left(\left|\vec{r} - \vec{R}_j\right|, \kappa\right), \quad (54)$$

whilst all the other states are doubly-degenerate with complex conjugated wave functions

$$\psi_n(\vec{r}) = C_1 \sum_{j=1}^M e^{-i(j-1)\frac{2\pi n}{M}} \cdot g\left(\left|\vec{r} - \vec{R}_j\right|, \kappa\right), \quad (55)$$

$$\psi_{\bar{n}}(\vec{r}) = C_1 \sum_{j=1}^M e^{i(j-1)\frac{2\pi n}{M}} \cdot g\left(\left|\vec{r} - \vec{R}_j\right|, \kappa\right), \quad n = 1, \dots, [M/2] - 1, \quad (56)$$

where the constant C_1 can be found from the normalization condition.

4.2 Continuous spectrum problem

Now we consider the scattering of plane wave incident axially on the M -atom potential plane symmetrical structure under question.

We write the solution to the Schrodinger equation as

$$\psi(\vec{r}) = A_0 e^{ikz} + \sum_{j=1}^M C_j \cdot g\left(\left|\vec{r} - \vec{R}_j\right|, -ik\right), \quad (57)$$

where $k = \sqrt{\frac{2\mu E}{\hbar^2}}$, A_0 is an amplitude of the incident plane wave and $g(r, \kappa)$ is as introduced above according to

(44).

As before (and using previously described notation), at each atom the solution must satisfy the ZRP condition

(11)

$$\left. \frac{\partial \log \left(\left| \vec{r} - \vec{R}_j \right| \cdot \psi(\vec{r}) \right)}{\partial \left| \vec{r} - \vec{R}_j \right|} \right|_{\left| \vec{r} - \vec{R}_j \right|=0} = \frac{1}{C_j} (A_0 + \dots + C_{j-1} \cdot g(\Delta R_1, -ik) + C_j \cdot ik + C_{j+1} \cdot g(\Delta R_1, -ik) + \dots) = -\beta.$$

This results in the set of linear equations

$$\begin{pmatrix} \beta + ik & g(\Delta R_1, -ik) & \dots & g(\Delta R_2, -ik) & g(\Delta R_1, -ik) \\ g(\Delta R_1, -ik) & \beta + ik & \dots & g(\Delta R_3, -ik) & g(\Delta R_2, -ik) \\ \dots & \dots & \ddots & \dots & \dots \\ g(\Delta R_2, -ik) & g(\Delta R_3, -ik) & \dots & \beta + ik & g(\Delta R_1, -ik) \\ g(\Delta R_1, -ik) & g(\Delta R_2, -ik) & \dots & g(\Delta R_1, -ik) & \beta + ik \end{pmatrix} \begin{pmatrix} C_1 \\ C_2 \\ \vdots \\ C_{M-1} \\ C_M \end{pmatrix} = -A_0 \begin{pmatrix} 1 \\ 1 \\ \vdots \\ 1 \\ 1 \end{pmatrix},$$

that obviously has the solution corresponding to trivial symmetry of the system

$$C_1 = \dots = C_M \equiv C_{0M}. \quad (58)$$

From any of the equation of the set it follows that

$$C_{0M} = \begin{cases} -\frac{A_0}{\beta + ik + 2 \sum_{j=1}^{(M-1)/2} g(\Delta R_j, -ik)}, & M - \text{odd}, \\ -\frac{A_0}{\beta + ik + 2 \sum_{j=1}^{M/2-1} g(\Delta R_j, -ik) + g(\Delta R_{M/2}, -ik)}, & M - \text{even}. \end{cases}$$

This can be unified as

$$C_{0M} = -\frac{A_0}{\beta + ik + 2 \sum_{j=1}^{(M+\chi_M)/2-1} g(\Delta R_j, -ik) + \chi_{M-1} \cdot g(\Delta R_{M/2}, -ik)}, \quad (59)$$

where $\chi_M = \frac{M/2 - [M/2]}{M/2 - [(M-1)/2]}$ is an indicator of parity of the number of atoms M .

It is also useful to recall (45) and rewrite the sum explicitly

$$\sum_{j=1}^{(M+\chi_M)/2-1} g(\Delta R_j, -ik) = \frac{1}{2R_0} \sum_{j=2}^{(M+\chi_M)/2} \frac{\exp(2ikR_0 \sin(\phi_j/2))}{\sin(\phi_j/2)} \quad (60)$$

with $\phi_j = \frac{2\pi}{M}(j-1)$.

Having obtained that, and taking into account the expansion $\left| \vec{r} - \vec{R}_j \right| \approx r - \frac{\vec{r}}{r} \cdot \vec{R}_j$ at $r \rightarrow \infty$, we can present

the solution (57) as

$$\psi(\vec{r}) = A_0 \left(e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right), \quad (61)$$

where the scattering amplitude at long distances in direction $\vec{n} = \vec{r}/r = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)^T$ is given by

$$f(\theta, \phi) = C_{0M}/A_0 \sum_{j=1}^M e^{-ik\vec{n} \cdot \vec{R}_j} = C_{0M}/A_0 \sum_{j=1}^M \exp \{ -ikR_0 \sin \theta \cos(\phi - \phi_j) \}. \quad (62)$$

From here the differential cross-section can be determined

$$\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2, \quad (63)$$

as well as the total scattering cross-section

$$\sigma = \int_0^{2\pi} \int_0^\pi |f(\theta, \phi)|^2 \sin \theta d\theta d\phi. \quad (64)$$

This also can be expressed according to the optical theorem

$$\sigma = \frac{4\pi}{k} \text{Im} \{ f(0, \phi) \}. \quad (65)$$

Therefore,

$$\sigma = \frac{4\pi M}{k} \text{Im} \{ C_{0M}/A_0 \} = \frac{4\pi M}{k} \frac{k + P}{(k + P)^2 + (\beta + Q)^2}, \quad (66)$$

where we denote

$$P \equiv \frac{1}{R_0} \cdot \left\{ \sum_{j=1}^{(M+\chi_M)/2-1} \frac{\sin(2kR_0 \sin(\pi j/M))}{\sin(\pi j/M)} + \frac{\chi_{M-1}}{2} \cdot \sin(2kR_0) \right\}, \quad (67)$$

$$Q \equiv \frac{1}{R_0} \cdot \left\{ \sum_{j=1}^{(M+\chi_M)/2-1} \frac{\cos(2kR_0 \sin(\pi j/M))}{\sin(\pi j/M)} + \frac{\chi_{M-1}}{2} \cdot \cos(2kR_0) \right\}. \quad (68)$$

We note that for the case of a single ZRP scatterer (i.e. $M = 1$) characterized by

$$\left. \frac{d \log(r\psi(r))}{dr} \right|_{r=0} = -\beta_0, \quad (69)$$

the formula (59) should be obviously replaced with

$$C_{01} = -\frac{A_0}{\beta_0 + ik} \quad (70)$$

resulting in the following formula for total scattering cross-section

$$\sigma = \frac{4\pi}{k} \text{Im} \{C_{01}/A_0\} = \frac{4\pi}{k^2 + \beta_0^2}. \quad (71)$$

As it was announced, we believe that a simplified theoretical model of molecular structures can be built by replacing each multiatomic molecule with some ZRP once its spectrum is known. Indeed, in particular for scattering on one molecule instead of (66) one would attempt to use (71) with β_0 to be chosen from the discrete spectrum levels κ_m according to the obtained formula (41).

4.3 Results for benzene molecule

Focusing on particular case of a benzene molecule C_6H_6 that can be considered as a cyclic structures formed by $C - H$ constituents described by ZRPs, we set $M = 6$ and start with the bounded state problem solution.

Structure of the discrete spectrum is as described by (53)-(56), i.e. there are 4 energy levels with 2 middle ones being doubly degenerate. Numerical solution of the transcendental equations (52) yields the values of energy levels which are compared with those obtained by the well-known Huckel method on the Fig. 3. The spectrum, namely distances between the energy levels, reveals good correspondence of ZRP approach to the qualitative Huckel calculations dictating energies from the ground to the highest level to be $E_0 - 2A$, $E_0 - A$, $E_0 + A$, $E_0 + 2A$, respectively [17, 6].

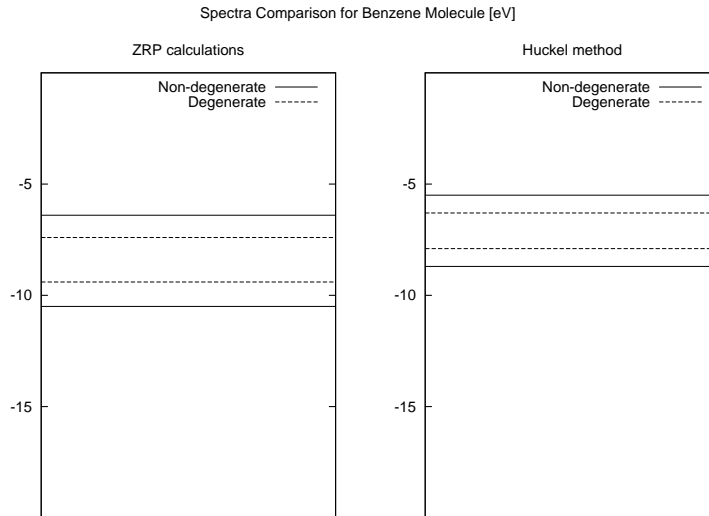


Fig. 3: Comparison of ZRP and Huckel calculations of energy levels for benzene molecule

To analyze continuous spectrum, we consider total scattering cross-section dependence on energy.

We compare the results given by the standard (atomic) ZRP model of the molecule (66) and those followed from single ZRP description of the molecule, i.e. (71) using the inverse of effective scattering length as introduced by (41). As one can observe on the plots given below for differently estimated values of radius of benzene molecule (e.g. see the introduction of [21]), there is moderate coincidence between conventional set of atomic ZRPs model and proposed single molecular ZRP approach.

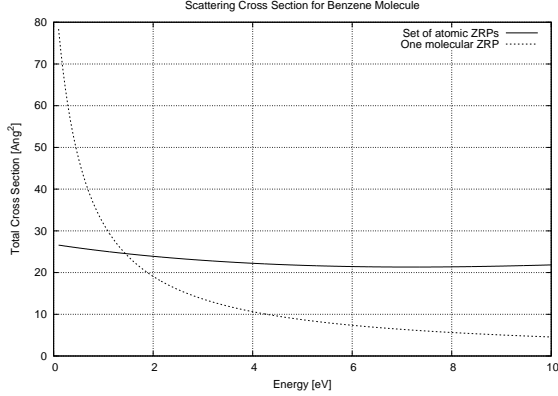


Fig. 4: Total scattering cross-sections for atomic and molecular ZRPs: smaller radius R_{01} of benzene molecule ($C - C$ bond length estimation).

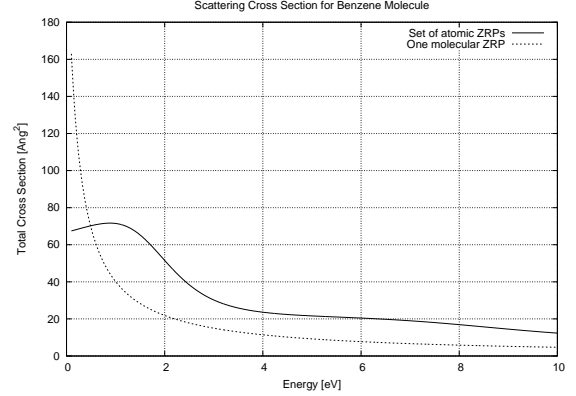


Fig. 5: Total scattering cross-sections for atomic and molecular ZRPs: bigger radius R_{02} of benzene molecule (effective upper estimation).

Also we notice that better correspondence of the molecular ZRP results to those obtained with the set of standard ZRPs can be achieved if in the dressing procedure one includes only the ground state and the state with maximal energy, i.e. $E_j = -\frac{\hbar^2 \kappa_j^2}{2\mu}$, $j = 0, 3$. This can be viewed as if we follow the described general procedure of application DT for every level, but for each doubly degenerated level with $E_j = -\frac{\hbar^2 \kappa_j^2}{2\mu}$, $j = 1, 2$ we perform an additional DT again with the prop function of type (25) but choosing a negative transformation parameter $\kappa = -\kappa_j$, $j = 1, 2$ (corresponding to the same energy level). This results in cancellation of consecutive contributions of the DTs with opposite to each other spectral parameters, hence the expression (41) gives

$$\beta = (\kappa_0^{-1} + \kappa_3^{-1})^{-1}, \quad (72)$$

This result is not surprising since, as it can be seen from the scattering matrix formalism, such pair of DTs yields consecutive adding and removal of a pole on the imaginary positive k half-axis (which corresponds to a bounded state) of (31): $s_0 \cdot \frac{k+i\kappa_j}{k-i\kappa_j} \cdot \frac{k-i\kappa_j}{k+i\kappa_j} = s_0$, $j = 1, 2$.

That is effective characteristic involves only the lowest and the highest energy level parameters. In case of odd number of atoms this would involve only the ground state energy parameter κ_0 .

Refined in this way molecular potential gives results demonstrated on the Fig. 6, 7.

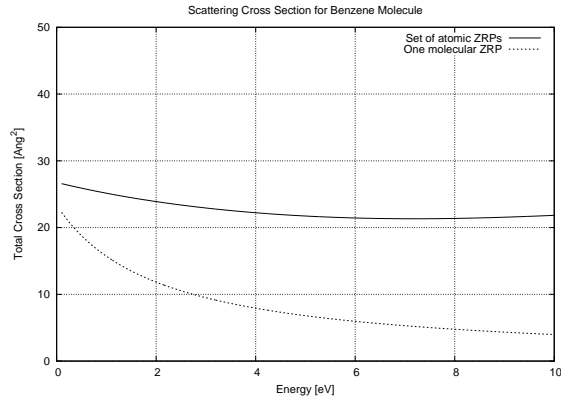


Fig. 6: Total scattering cross-sections for atomic and molecular ZRPs: smaller radius R_{01} of benzene molecule, level degeneracy is taken into account.

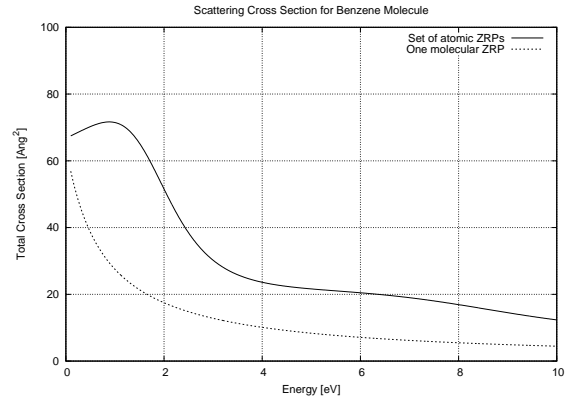


Fig. 7: Total scattering cross-sections for atomic and molecular ZRPs: bigger radius R_{02} of benzene molecule, level degeneracy is taken into account.

Below is the table with values of parameters used for calculations of data presented on the Fig. 3 - 7.

β	E_0	A	R_{01}	R_{02}
1.5 Ang^{-1}	-7.1 eV	0.8 eV	1.4 Ang	3.6 Ang

Table 1. Set of parameters for data plotted on the figures.

5 Conclusions

The presented method of extension of conventional atomic ZRP approach is made to describe molecular structures based on their discrete spectrum. Bounded state energies, either found from conventional ZRP calculations or in whatever alternative way, determine effective characteristic of newly introduced single ZRP that is expected to adequately describe properties of a molecule.

Certainly, replacement of arbitrary molecules with spherically symmetric point-centers is a crude approximation valid only in low-energy limit, however, as it was demonstrated, even in case of highly anisotropic molecules, like benzene, the model gives not perfect but reasonable quality results at the same time allowing significant simplification in formulation of more complicated molecular structures problems with molecules instead of atoms as ZRP constituents. Although we believe that the molecular ZRP method should be tested on more examples in order to prove its quantitative merit, it seems to be a beneficial tool at least to obtain estimates of results on physically reasonable analytical grounds.

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